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# Surface science investigations of photoprocesses in model interstellar ices

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The kinetic energy of benzene and water molecules photodesorbed from astrophysically relevant ices on a sapphire substrate under irradiation by a UV laser tuned to the  $S_1 \leftarrow S_0 \pi \rightarrow \pi^*$  transition of benzene has been measured using time-of-flight mass spectrometry. Three distinct photodesorption mechanisms have been identified—a direct adsorbate-mediated desorption of benzene, an indirect adsorbate-mediated desorption of water, and a substrate-mediated desorption of both benzene and water. The translational temperature of each desorbing population was well in excess of the ambient temperature of the ice matrix. © 2008 American Vacuum Society. [DOI: 10.1116/1.2834687]

## I. INTRODUCTION

In the past few decades, the astronomy and astrophysics communities have come to realize that physical and chemical processes occurring at the surfaces of interstellar dust grains play a key role in the chemical evolution of the universe.<sup>1</sup> Grain surfaces promote the formation of molecular hydrogen and simple hydride species such as water, ammonia, and methane. Icy mantles are accreted on dust grains at the low temperatures ( $\leq 20$  K) prevalent in the chemically rich molecular clouds by a combination of such reactions and condensation from the gas phase, and are readily observed along many lines of sight.<sup>2</sup> During the early phases of star formation, these mantles play a crucial role as reservoirs for small molecular coolants which promote the formation of small, long-lived stars such as our own Sun.<sup>3,4</sup> Studies of the chemical evolution of water-rich icy mixtures during irradiation by light and charged particles have been reported in numerous publications. Few, if any, have examined the distribution of energy between chemical changes and physical processes such as light emission, particle desorption, and morphological change (Fig. 1). Here, we present the first

results of a project designed to address this issue, initially focusing on photodesorption from layered ices of water and benzene. Water is the most abundant molecule in icy grain mantles.<sup>5</sup> Benzene has been chosen as an experimentally convenient representative of the polycyclic aromatic hydrocarbon (PAH) family. PAHs are thought to be ubiquitously present in the interstellar medium,<sup>6</sup> and are likely to exist in the presence of water ice as either a component of icy mantles or as part of the carbonaceous component of the dust grain itself.

Photodesorption is potentially an important process in a variety of astrophysical environments. It is often invoked to account for the high gas-phase abundances of less volatile molecules, such as water, that are observed under conditions where complete freeze-out onto dust grains might otherwise be expected.<sup>7,8</sup> However, only a few experimental studies of photodesorption with an astrophysical context have been performed.<sup>9–11</sup> These have measured photodesorption rates of water and CO under Lyman  $\alpha$  radiation. In contrast, this study focuses on the energetics of the photodesorption process. Photodesorption of PAHs under UV irradiation has not previously been studied in an astrophysical context, although there are a few published studies of IR laser promoted photodesorption from benzene, PAH, and water ice films.<sup>12–14</sup>

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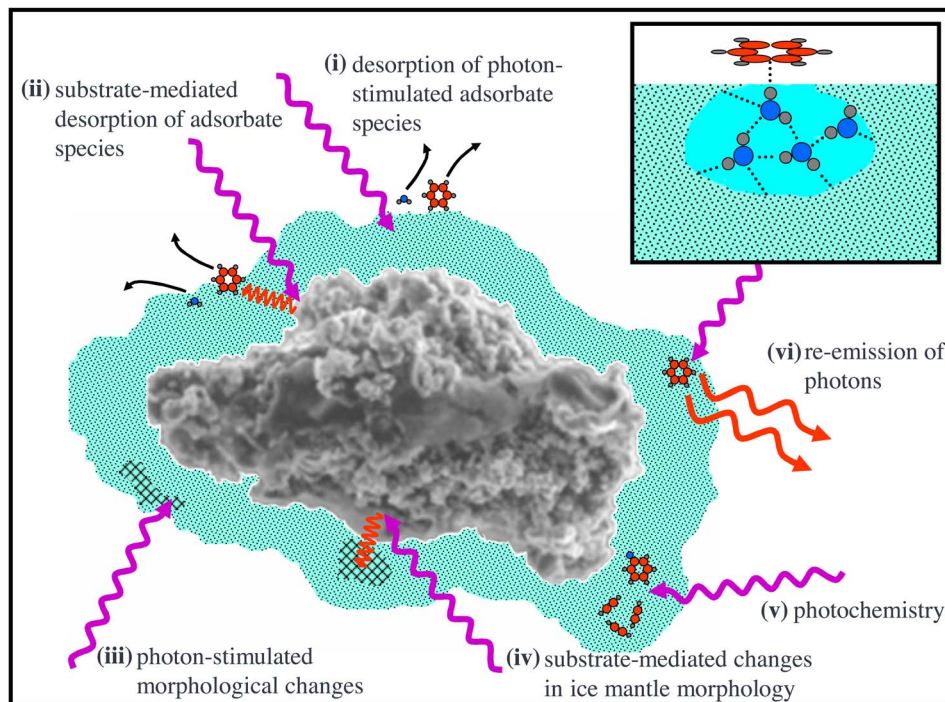


FIG. 1. A cartoon illustrating the potential range of processes that might occur within a PAH doped water ice matrix subject to irradiation with UV photons. The inset shows a molecular scale cartoon of a surface bound benzene and its associated hydrogen-bonded cluster, the unimolecular decomposition of which yields the hot benzene, and water in the gas phase. Dust grain image adapted from <http://presolar.wustl.edu/work/idp.html>

## II. EXPERIMENTAL PROCEDURES

Experiments were performed in the dedicated ultrahigh vacuum (UHV) chamber (base pressure =  $1 \times 10^{-10}$  mbar) in the Central Laser Facility (CLF) at the Rutherford Appleton Laboratories (RAL).<sup>15</sup> Analytical grade benzene and de-ionized water were purified by freeze-pump-thaw cycles. Sequential deposition of benzene and water layers onto a sapphire crystal (1 mm  $\times$  10 mm diameter) at a temperature of  $\sim 80$  K was performed by backfilling the chamber to a pressure (uncorrected ion gauge) of  $4 \times 10^{-7}$  mbar for 500 s. From literature values of the densities of amorphous solid water<sup>16</sup> and solid benzene,<sup>17</sup> film thicknesses of 21 and 7 nm, respectively, are estimated, assuming a sticking probability of unity. Depositions of this size provide a convenient compromise between desorption signal and experiment duration (pump down time). Layered systems avoid the complexity of composition and temperature dependent variations in absorbance of benzene/water mixtures at the chosen wavelengths of irradiation.<sup>18</sup> We denote the layer configurations as follows: benzene on sapphire alone (S/B); water alone (S/W); sequential adsorption of benzene followed by water (S/B/W); sequential adsorption of water then benzene (S/W/B).

The films were irradiated with the frequency-doubled output of a nanosecond pulsed Nd<sup>3+</sup>-YAG (YAG denotes yttrium aluminum garnet) pumped dye laser, incident at an angle of  $45^\circ$  and focused onto an area of approximately 0.5 mm<sup>2</sup>. The laser was operated with a pulse frequency of 10 Hz, and pulse energies of either 1.8 or 1.1 mJ, corresponding to irradiances of 360 or 220 mJ cm<sup>-2</sup> per pulse. The pulse-to-pulse variation in the irradiance was typically about  $\pm 10\%$ . Molecules desorbing normal to the surface were detected by a pulse counting quadrupole mass spectrometer, after flying down a liquid nitrogen cooled line-of-

sight tube.<sup>19</sup> The benzene and water molecules were detected by their parent ions of mass 78  $m_u$  and 18  $m_u$ , respectively. The time-of-flight (ToF) of the desorbed molecules was measured with a resolution of 2.56  $\mu$ s over a range of 0–42 ms, by a multichannel scaler which was triggered after each laser pulse. Data were accumulated for 200 laser pulses, after which time no further signals were observed in any experiments. Data were typically averaged over 30 spots from different locations on the sample surface. The ToF profiles were fitted with a density weighted Maxwell-Boltzmann (M-B) function<sup>20</sup> to determine the translational temperature  $T_t$  of the desorbed molecules.

Experiments were conducted at three laser wavelengths. The “on-resonance” wavelength of 250.0 nm was chosen to excite one of the several vibronic components of the  $B_{2u} \leftarrow A_{1g}$  transition of benzene; a  $\pi(1e_{1g}) \rightarrow \pi^*(1e_{2u})$  promotion of an electron in the aromatic ring of the molecule. The widths and precise positions of the vibronic components of this transition in solid benzene have been found to vary with temperature, particularly around the adsorption temperature.<sup>18</sup> We have chosen 248.8 nm as a “near-resonance” wavelength, as we believe it to be close to a non-negligible local minimum in the absorption cross section of benzene. The absorption cross section varies between 4.5 and  $1.2 \times 10^{-22}$  m<sup>2</sup> at the maximum and minimum of the peak, and is two orders of magnitude lower at the “off-resonance” wavelength of 275.0 nm.<sup>18</sup> The absorption cross section of water ice is negligible over the entire wavelength range.<sup>21</sup> However, sapphire has a small but significant absorbance over this range.<sup>22</sup> Based on these absorbance values, it is estimated that 4% and at most 6% of the photon flux at 250.0 nm is absorbed by the sapphire substrate and the benzene layer, respectively. We therefore expect substrate-

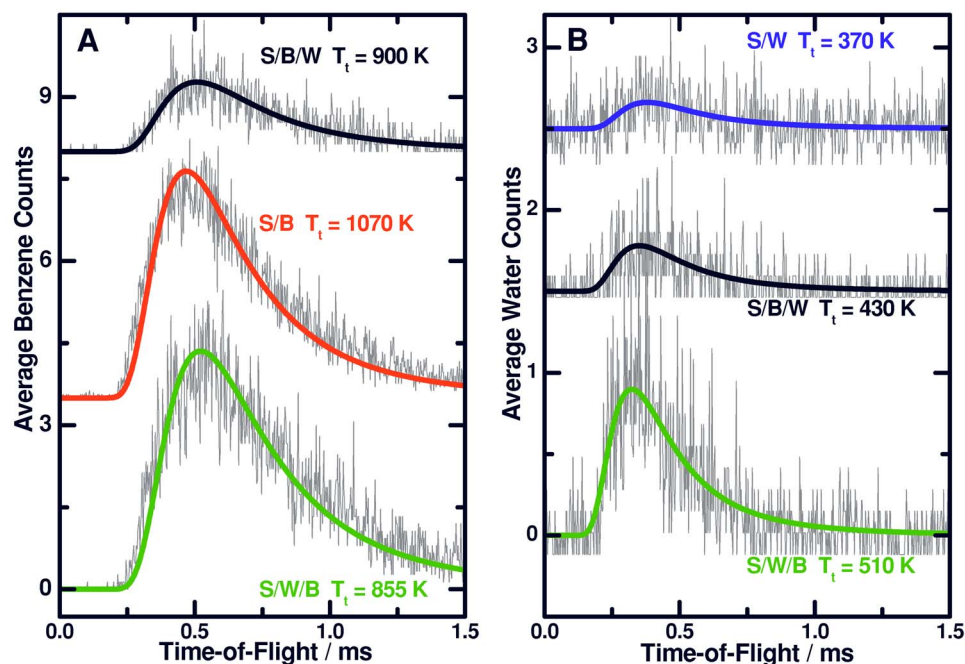


FIG. 2. ToF profiles of (a) benzene and (b) water desorption for varying layer configurations, following excitation at 250.0 nm with 1.8 mJ per pulse of optical energy. Thin gray lines: raw data; thick lines: single component M-B fits. Profiles have been offset for clarity.

mediated processes due to heating of the sapphire to have an important influence on the results. The irradiance at both pulse energies is above the reported threshold for ablation of benzene.<sup>23</sup> However, the laser ablation threshold is known to rise as the film thickness decreases from a value equivalent to the penetration depth of the laser.<sup>24</sup> Therefore, with only a small fraction of the incident radiation absorbed by the thin benzene film, the effective values of irradiance are too low to result in an ablation process.

### III. RESULTS

The on-resonance ToF profiles for photodesorbed benzene and water from varied layer configurations are shown in Fig. 2. Both benzene and water exhibit a single desorption peak from each configuration in which they were present. However, there is some variation in the size and precise position of the peaks between configurations. Film morphology is expected to play a role in this variation, as illustrated in Fig. 3. For the S/B/W system, desorption of benzene is inhibited by the presence of the thick overlayer of water ice, hence, the desorption rate is lower compared to the S/B system. Amor-

phous water ice deposited at 80 K is known to have an uneven surface, resulting in a high surface area.<sup>25</sup> Furthermore, benzene tends not to wet the surface of water, instead forming three dimensional clusters upon adsorption.<sup>26</sup> Therefore, the rate of benzene desorption in the S/W/B system can be expected to be greater than that of the S/B system due to the larger surface area available for benzene adsorption. Desorption of water was observed in the absence of benzene and is attributed to a substrate-mediated mechanism. Water desorption is enhanced in the presence of benzene. Therefore, an indirect adsorbate-mediated process must also be operating, in which the energy absorbed by the benzene molecules is transferred to the water molecules causing them to desorb. The enhancement is slight for the S/B/W system, but much greater for the S/W/B system. In the S/B/W system, excited molecules must escape from the B/W interface through the thicker water overlayer. In the S/W/B system, the thinner benzene overlayer poses much less of a barrier, and the rate of water desorption is correspondingly higher.

Figure 4 displays the wavelength dependence of the photodesorption of benzene from the S/B system and water from the S/W/B system. At the off-resonance wavelength, benzene desorption is evident, which again indicates that a substrate-mediated desorption mechanism is operative. A single component M-B fit gives a translational temperature of 530 K. As expected, the benzene desorption is much more intense at the on-resonance wavelength. The on-resonance peak is also slightly faster than the off-resonance peak. This desorption peak is therefore thought to arise from a combination of the direct adsorbate-mediated and the substrate-mediated desorption mechanisms. While a single component routine provides an adequate fit to each benzene ToF profile, we have applied a two component fitting routine to the on-resonance and near-resonance peaks in order to derive a temperature for the

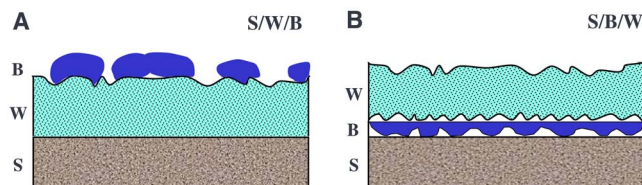


FIG. 3. Cartoon summarizing the expected morphology of the layers of ice in each of the deposition configurations studied (not to scale). (a) S/W/B system: water wets the surface of the sapphire; the thinner layer of benzene does not wet the water and forms islands on its rough surface. (b) S/B/W system: the thin layer of benzene does not wet the sapphire; the thicker overlayer of water does not wet the surface of the thin benzene layer.



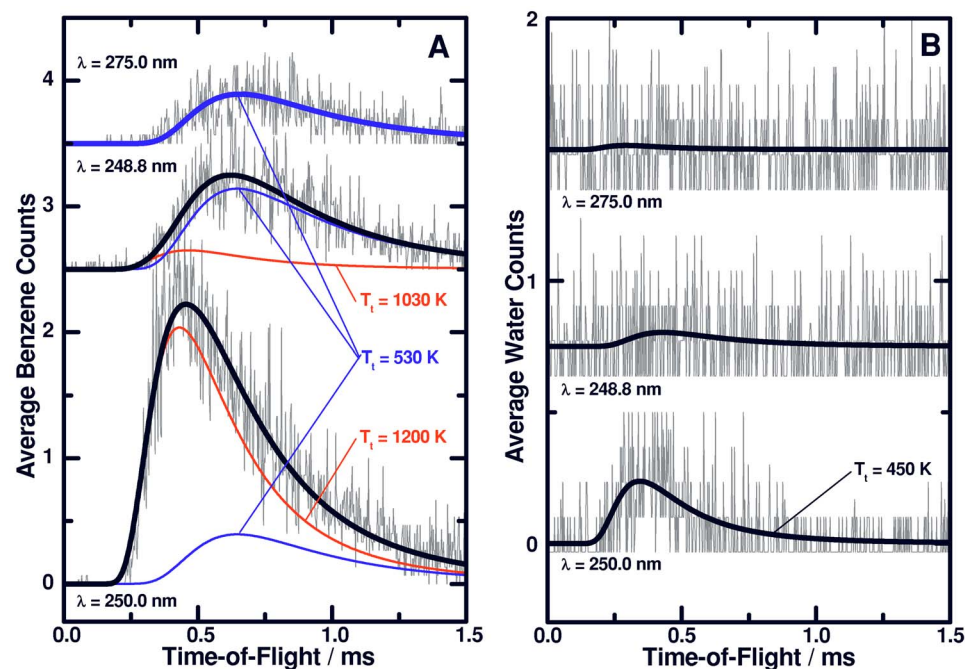


FIG. 4. (a) ToF profiles of benzene desorption from the S/B system as a function of photon wavelength at an optical power of 1.1 mJ per pulse; thin gray lines: raw data; thick lines: M-B fits, one component fixed at  $T_i = 530$  K, one free component, and the sum of the two components. (b) ToF profiles of water desorption from the S/W/B system as a function of photon wavelength at an optical power of 1.1 mJ per pulse; thin gray lines: raw data; thick lines: single component M-B fits. Profiles have been offset for clarity.

direct adsorbate-mediated mechanism. The temperature of one component was fixed at 530 K, reflecting the contribution of the substrate-mediated channel, while the temperature of the second component and the intensities of both components were allowed to vary. The size of the 530 K component was found to be similar in each experiment, as is expected for a substrate-mediated process which is relatively insensitive to the photon wavelength, since the sapphire absorption cross section itself is relatively constant in this wavelength region. For the on-resonance experiment, the free component which we assign to the adsorbate-mediated desorption of benzene dominates the ToF profile, having a much higher translational temperature of 1200 K. The two component fit to the near-resonance data produces a small peak for adsorbate-mediated desorption at 1030 K. After averaging the fitted temperatures weighted against the size of the component over all of the benzene desorption experiments, we find the translational temperature of benzene desorbed by the direct adsorbate-mediated and substrate-mediated mechanisms to be  $1200 \pm 200$  and  $530 \pm 100$  K, respectively. A single component fit to the on-resonance water desorption from the S/W/B system gives a translational temperature of 450 K. However, at the lower laser power, the rates of water desorption at near resonance and off resonance shown were too low to obtain a meaningful temperature fit, as demonstrated in Fig. 4(b). Although we have concluded from the results in Fig. 2(b) that two mechanisms for water desorption are operating, no significant differences in the translational temperature were apparent. Water desorption by both indirect adsorbate-mediated and substrate-mediated mechanisms occur at a similar temperature, which when averaged over all of the experiments performed, was found to be  $450 \pm 100$  K.

A much slower water desorption peak was also evident in some experiments, although its presence, position, and intensity did not show good spot-to-spot reproducibility. A M-B fit gives an unphysical translational temperature of less than 1 K. As is illustrated in Fig. 5(a), this slow desorption was only evident for the S/B/W system. As shown in Fig. 5(b), the peak was largest at the on-resonance wavelength and absent in the off-resonance experiment, demonstrating that this feature results from resonant benzene absorption, rather than a substrate-mediated process. We believe that this peak may be due to desorption of water clusters that disintegrate within the mass spectrometer to contribute to the water monomer signal at mass  $18m_u$ . The disintegration of such clusters may add an additional time delay, which, when contributing to the apparent ToF of detected water molecules, prevents us from obtaining a sensible M-B fit to the peak. Interestingly, there is no evidence for an equivalent slow feature in the benzene ToF data, suggesting that these clusters contain only water molecules and no benzene. Further experiments are required to confirm the desorption of water clusters as the origin of this slow signal.

#### IV. DISCUSSION

Three distinct photodesorption mechanisms can be identified from the results presented here. First, desorption can occur following absorption of a photon by an adsorbate molecule: *direct adsorbate-mediated photodesorption*. Second, desorption can occur following energy transfer from a neighboring adsorbate molecule which has been excited by absorption of a photon: *indirect adsorbate-mediated photodesorption*. Third, desorption can occur following transfer of energy absorbed by the substrate: *substrate-mediated photo-*

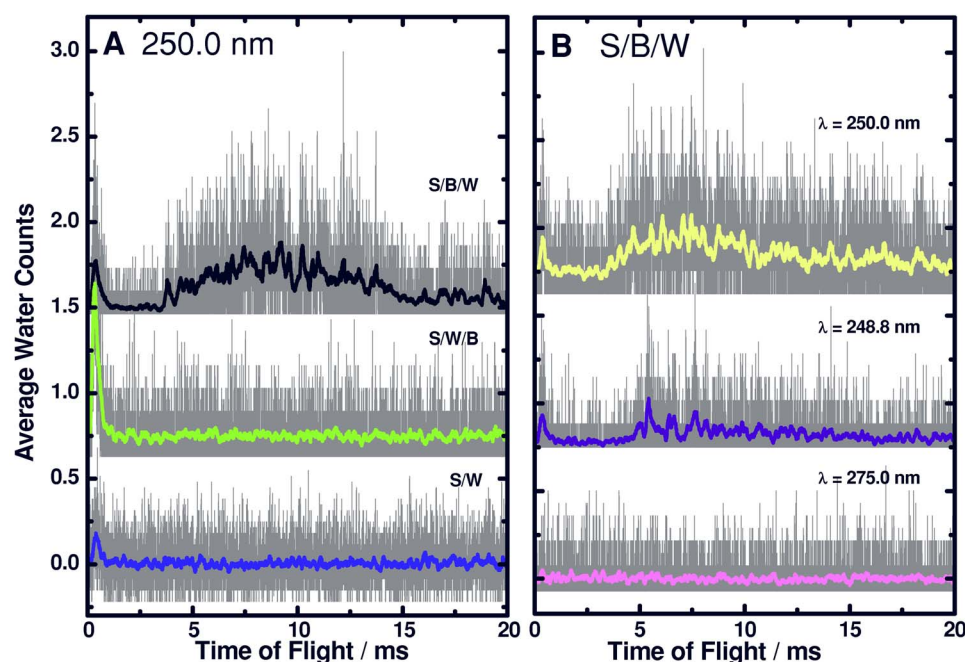


FIG. 5. Extended ToF profiles of water desorption, (a) from varying layer configurations at 250.0 nm (pulse energy = 1.8 mJ), and (b) from the S/B/W system at varying wavelength (pulse energy = 1.1 mJ). Thin gray lines: raw data; thick lines: 48 point adjacent average smoothed data.

*desorption.* For each mechanism, the  $T_t$  of the photodesorbed molecule, be it benzene or water, is much higher than the temperature of the ice matrix from which it desorbed.

To interpret this behavior, at least for the direct adsorbate-mediated desorption of benzene, we introduce a simple *a priori* statistical model which assumes that each exit state is equally probable.<sup>27</sup> Benzene is known to hydrogen bond via its  $\pi$  system to strong proton donors such as water.<sup>28–30</sup> We consider benzene adsorbed on the water surface to be connected to a cluster of  $x$  water molecules via a single water molecule through such a  $\pi$  facial hydrogen bond, as shown in the inset of Fig. 1. The strength of this hydrogen bond for benzene adsorbed on an amorphous water surface is estimated to be  $18.0 \text{ kJ mol}^{-1}$ ,<sup>31</sup> which represents the activation energy in the unimolecular decomposition of this surface complex. The average kinetic energy release (KER) in such a large system can then be written,<sup>25,32</sup>

$$\langle E_k \rangle = 2 \frac{E_{\text{int}} - E_a}{s - 1},$$

where  $E_{\text{int}}$  is the internal energy of the system,  $E_a$  the activation energy, and  $s$  is the number of degrees of freedom over which the energy is spread. For a  $\text{C}_6\text{H}_6 \cdots (\text{H}_2\text{O})_x$  cluster,  $s$  has a value of  $3n - 6$ , where the number of atoms,  $n$ , is  $12 + 3x$ . Hence,  $s$  takes a value of  $30 + 9x$ . From the kinetic temperature of the benzene derived from our ToF measurements, we estimate the KER to be  $9.98 \text{ kJ mol}^{-1}$ . Let us then assume that rapid intermolecular vibrational energy relaxation in the condensed phase brings the benzene to the lowest vibrational state in  $S_1$  ( $B_{2u}$ ) whereupon unimolecular dissociation occurs following internal conversion on to the  $S_0$  ( $A_{1g}$ ) manifold. This corresponds to a benzene molecule with an internal energy of approximately  $460 \text{ kJ mol}^{-1}$ . With this information, we can estimate  $x$  to be approximately seven;

i.e., the benzene molecule is bonded to a surface cluster of approximately seven water molecules. We are confident that this simple *a priori* model can explain the energy released into benzene and into water molecules (assuming sequential decomposition of the surface cluster) and we are currently in the process of modeling our observed ToF distributions on this basis.

Under the conditions of low photon flux prevalent in astrophysical environments, only single-photon processes can occur. Comparison of results at two pulse energies show that, within experimental error, the rates of both benzene and water photodesorption scale linearly with photon flux, which is consistent with a single-photon process. Water films on a graphite surface were found to desorb via a multiphoton process when irradiated with photons in the 275–670 nm range.<sup>33</sup> However, desorption was limited to 0.25 ML (monolayer) of water molecules at the film surface. It is unlikely that photodesorption by this mechanism could be detected using our experimental design. In contrast, irradiation of a  $200 \mu\text{m}$  thick water film at 248.0 nm gave rise to an unlimited yield of photodesorbed water molecules with a  $T_t$  of 770 K, via a two-photon process.<sup>34</sup> Although our experimental conditions are comparable with the lowest photon fluxes in this previous study, the absence of any population of desorbed water molecules with a  $T_t$  near to 770 K suggests that the cross section for this two-photon process is too low to produce a significant photodesorption yield from a water film of some four orders of magnitude lower in thickness.

The measurements of the two adsorbate-mediated photodesorption mechanisms reported here have explicit relevance to astrophysical environments. While the sapphire crystal is not an ideal representation of an interstellar dust grain, the observation of a substrate-mediated photodesorption mechanism demonstrates that absorption by silicate and metal ox-

ide components of real dust grains will likely contribute to photodesorption in astrophysical environments. Although we have thus far examined absorption by only a single band of the benzene molecule, we believe it to be likely that photodesorption of suprathermal molecules will generally be the case, regardless of the desorbate species or the absorption band, provided that sufficient energy is deposited into the desorption coordinate to exceed the thermal desorption energy. The high  $T_i$  of the desorbed molecules may influence gas-phase astrochemistry, by providing a means for molecules to overcome reaction barriers which would be otherwise insurmountable at the low ambient temperatures within molecular clouds. The implications for astrochemistry are discussed in more detail elsewhere.<sup>35</sup>

## V. CONCLUSIONS

Photon-stimulated desorption from layered benzene and water ices has been measured, revealing three single-photon desorption mechanisms. Benzene is photodesorbed with a  $T_i$  of around 1200 K via a direct adsorbate-mediated process following excitation of the  $B_{2u} \leftarrow A_{1g}$  transition. Water is photodesorbed with a  $T_i$  of  $\sim 450$  K via an indirect adsorbate-mediated process following excitation of the same benzene transition. Benzene and water are photodesorbed with a  $T_i$  of 530 and 450 K, respectively, via a substrate-mediated process following absorption of photons by the sapphire substrate.

Future experiments will aim to quantify rates of photodesorption in addition to energetic measurements, and also study photon-chemistry and photon-induced changes in ice morphology. A range of experimental parameters must be investigated to establish the influence of ice temperature, film thickness, structure (configuration), and mixture composition on photon-stimulated processes. A rigorous investigation of the flux dependence on the observed processes is essential to ensure that they occur via astrophysically relevant single-photon mechanisms. Studies targeting various absorption bands of a range of PAH molecules are planned.

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